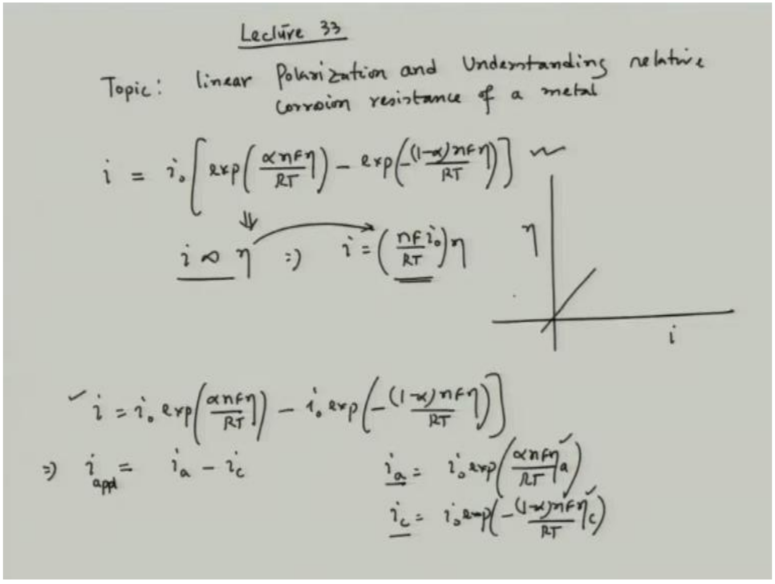
Corrosion - Part II

Prof. Kallol Mondal
Department of Materials Science and Engineering
Indian Institute of Technology - Kanpur

Lecture - 33
Linear Polarization and Understanding Relative Corrosion Resistance of a Metal

Hello everyone. Let’s start lecture 33.

(Refer Slide Time: 00:18)



Lecture 33

Topic: linear Polarization and Understanding relative corroion resistance of a metal

$$i = i_o\left[\exp\left(\frac{\alpha nF\eta}{RT}\right) - \exp\left(-\frac{(1-\alpha)nF\eta}{RT}\right)\right]$$

$$\Downarrow$$

$$\underline{i \propto \eta} \Rightarrow i = \left(\underline{\frac{nFi_o}{RT}}\right)\eta$$

$$i = i_o\exp\left(\frac{\alpha nF\eta}{RT}\right) - i_o\exp\left(-\frac{(1-\alpha)nF\eta}{RT}\right)\Big]$$

$$\Rightarrow i_{appl} = i_a - i_c$$

$$\underline{i_a} = i_o\exp\left(\frac{\alpha nF\eta_a}{RT}\right)$$

$$\underline{i_c} = i_o\exp\left(-\frac{(1-\alpha)nF\eta_c}{RT}\right)$$

And in the, at the end of lecture 32, we started discussing linear polarization and where we have found out an important relation that i which is the current density is proportional to the over voltage. And that is possible when over voltage is very, very small. So, we will continue our discussion on this linear polarization and try to find out a relation which can indicate a relative corrosion response of a metal in an electrolyte.

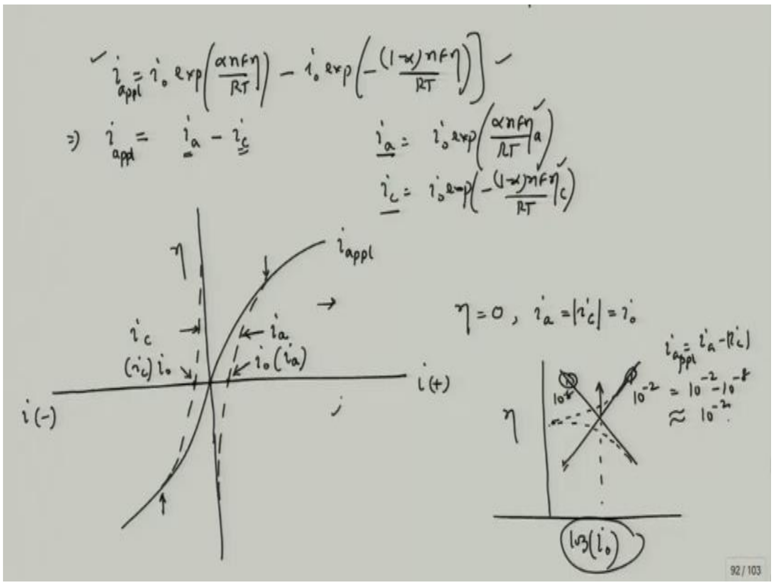
So, our discussion topic would be, linear polarization and understanding relative corrosion resistance of a metal in an electrolyte. Of course, relative means, of course in comparison to another metal. So now, we started with this Butler-Volmer equation, $i_o$exp[αnf/RT]. This was the equation we started with. And then finally, we have achieved this relation where

$$i = \frac{nF\, i_o}{RT}\eta$$

So, this is basically the constant which is giving a linear relation. And we have also seen that if we try to plot i over voltage, so it will be linear. Now, if we see this particular equation, I can break into 2 terms. i + i_o exponential, this term. This 2 terms we can explain. And then, I can write it as ic. And of course, that time, it is nothing but i applied or i circuit. So, this is, you so, ia + i zero exponential. I can write it as anodic over voltage.

And this is cathodic over voltage. This of course a cathodic over voltage. And this is cathodic current density, anodic current density. Now, if I try to plot this equation, not in the log scale of I, rather than absolute i with reference to over voltage, then the plot nature would be;

(Refer Slide Time: 04:30)



$$i_{appl} = i_0 \exp\left(\frac{\alpha nF\eta}{RT}\right) - i_0 \exp\left(-\frac{(1-\alpha)nF\eta}{RT}\right)$$

$$\Rightarrow i_{appl} = i_a - i_c$$

$$i_a = i_0 \exp\left(\frac{\alpha nF\eta_a}{RT}\right)$$

$$i_c = i_0 \exp\left(-\frac{(1-\alpha)nF\eta_c}{RT}\right)$$

$$\eta = 0, \; i_a = |i_c| = i_0$$

$$i_{appl} = i_a - |i_c|$$

$$10^{-2} - 10^{-8}$$

$$\approx 10^{-2}$$

This is i positive; this is i negative. Now, this positive, negative does not mean that the values are positive and negative. So, this positive, negative indicates the direction. So now, if I plot neeta with reference to i. And these equation gives me a plot like this. So, this is the plot pattern which indicates the plot of i applied. This is i applied. Now, I can individually check the current value, the plot of ia and as well as ic.

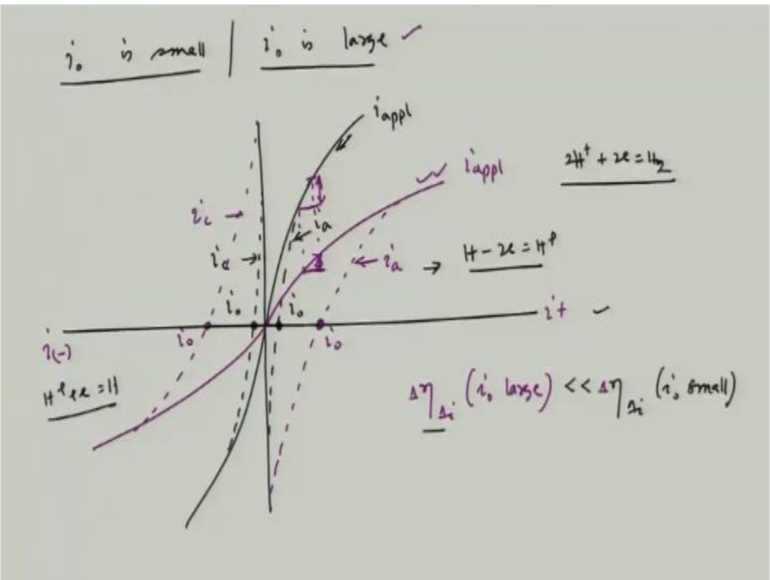
And if we see the plot, the plot would be looking like this. Fine. So, this is ia; this is ic. And if we see this; so, when neeta over voltage is zero, ia + ic + i zero. And here of course, I am taking the values. So now, this is, i zero also, this is i zero, but this is on the positive side and this is on the negative side. That means, at over voltage, the system is reaching non-corroding reversible condition.

And that too also steady condition. And then, as we go positive direction or negative direction in the over voltage axis, we get the individual current response. And interestingly, if you see, at a high current values in this direction, at this point, ia becomes + i applied. On the negative side, at this point, ic becomes i applied. This is also understandable, because, if we see the Evans diagram, we have seen that this was the over voltage plot, this was i zero.

And in this case, this was in the log scale, isn't it? So, that time, if you see this, the plot was like this, polarization plot. And as we go upward, since it is a log scale, I could see that influence of this quantity on this will be extremely low, because this is in the log scale. So, if this becomes 10^{-2} and this becomes 10^{-8}. So, the ia would be or i applied would be equal to ia + ic, which is 10^{-2} - 10^{-8}, which is almost equal to 10^{-2}.

So, that means, ia becomes equal to i applied. The similar thing applies here. So, that is what a higher over voltage i individual current densities would become equal to i applied So, this is the plot. Now, if I try to see the plot pattern;

(Refer Slide Time: 08:14)



When i zero is small and when; and another situation i zero is large. So, if I try to plot this i zero is large, that case, what could be the plot pattern? And when i zero is less is small, what could be the plot pattern? Now, if I try to see that; so, in one case i zero is small, so the plot will be very steep. And this is ia; this is ic. And this points are i zero values. Now, in another situation where i zero is large, this will be much more flattened.

And that case; So, this becomes ia; this becomes ic; and this is the i applied. And in other case, this is i applied; this is ia; this is ic. Now, interesting part is, if you see this, these 2 points are also equal. This is i zero; this is i zero two. For a second process where i zero is large. Now, this particular plot has got a meaning. If we see this plot, let's say I have some current fluctuation in the system.

This is current value, i+, i-. So now, if we have a small current perturbation, let's say this is my small current perturbation. Now, that time, if we have small current perturbation, my polarization amount would be this much. This much would be my polarization amount. Let's say, the same perturbation, if I give it to the case where i zero is small, this my is my small current perturbation.

And then, potential difference would be this much. So, that means, we could see that neeta over voltage for del i in case of i zero large is smaller neeta del I, i zero small. So now, that means, if i zero is very large for that reversible process, let's say if I consider this process. Let's say I consider hydrogen evolution reaction,

$$2H^{+} + 2e = H_2$$

For this process, in one case i zero is very large; in another case, i zero is very small.

And now, this side is indicating of H_2 - 2e = $2H^{+}$. And this side is $2H^{+}$ + 2e = H_2. So, this is cathodic, this is anodic process. Now, it means that, if we try to design an hydrogen, a hydrogen standard cell or a reference cell with a metal having very large i zero, even there is a small amount of current perturbation because of the process that is going on. So, we could see that over voltage change; instead of writing over voltage, so I can write this.

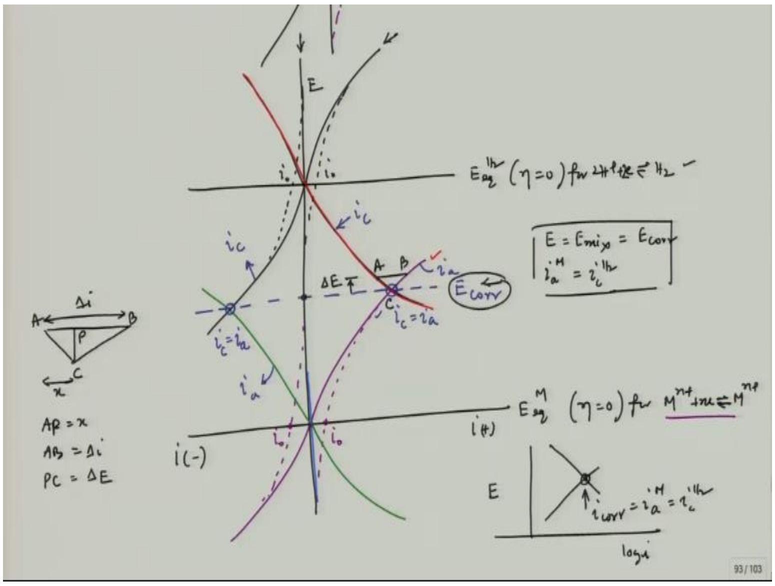
The change in voltage due to a small current perturbation in the system, for the case, for this case where i zero is large, the potential is much stabler than the potential for the case where i zero is small, for this situation, this case. So, if I have, if I one need to design a reference electrode out of some metal where hydrogen evolution reaction will reach a steady state and non- corroding condition or reversible condition; that case, I would always prefer a metal over which i zero is very large.

So, that case, even if I have a small current perturbation within its measurement terrain, I will not be able to have a much of change in a potential. So, if I do not have much of change in the potential, that means, I will be able to measure a potential of another electrode or in another reduction or another electrochemical process, with reference to this reference electrode.

So, it will be a much more stable electrode, stable hydrogen reference electron. So, that is what platinum is used while designing hydrogen reference electrode, because it has a higher i zero as compared to other metals. And platinized platinum is used because it increases the i zero. And once it has a higher i zero, the potential becomes much more stable. And for a reference electrode, you always need an electrode with a stable potential, which should not change with its small current perturbation within its measurement region.

So, that is the importance of this particular plot. Now, if I try to see a corrosion of metal; and let's say we are talking about corrosion of metal when hydrogen evolution reaction on it is the cathodic reaction. Then also, we can describe that corrosion process over this over voltage versus current plot. So, let's see how we are doing it. So, if I say this.

(Refer Slide Time: 15:12)



So, let's say this is the hydrogen equilibrium potential. Let's say this is over voltage. And I can also term it as in the form of potential. So, this becomes E equilibrium hydrogen. And let's say this is the E equilibrium of that metal. And this would be neeta + zero, for this reaction. And this would be equal to zero, for this reaction. So now, both of them have their own Butler-Volmer Equation.

Now, if I try to see the plot for this reaction to this reaction will be plotted like this, let's say. So, this is the plot. And for metal, let's say this becomes my plot. So, this is the 2 plots. And individual current density plot would be like this. So, this is i zero for metal. And now, for hydrogen evolution reaction, this becomes my individual current density. That means, ic and ia for hydrogen evolution.

So, this is i zero for hydrogen evolution. And this is the i zero, the second one, this particular case; these are the i zeros for metal, this particular reaction or electrochemical process. Now, in case of Evans diagram, what we have noticed; we have to reach to a situation where I could have a mixed potential. And there; so, that means I should reach E + E mix, which is nothing but E corr.

And that time, ia metal + ic hydrogen. So, this condition is to be met. And in case of Evans diagram, what how did I, how did we do it? So, we have log i and E. We have reached to this point. And this point becomes i corr + ia metal + ic hydrogen. So, that was the plot we had. So now, if I put a mirror on this particular plane, then actually what I can do, I can have a mirror image of this particular line.

So, if I do that mirror image; so, this is a mirror image. So, you if I plot this mirror image in red color, so this will be the mirror image. And for this, I can put a mirror here. And then, I can have a mirror image. So, the mirror image of this, if I try to draw it with a green color, so, it would be this and this. So, now I could see that they are meeting at this corrosion potential.

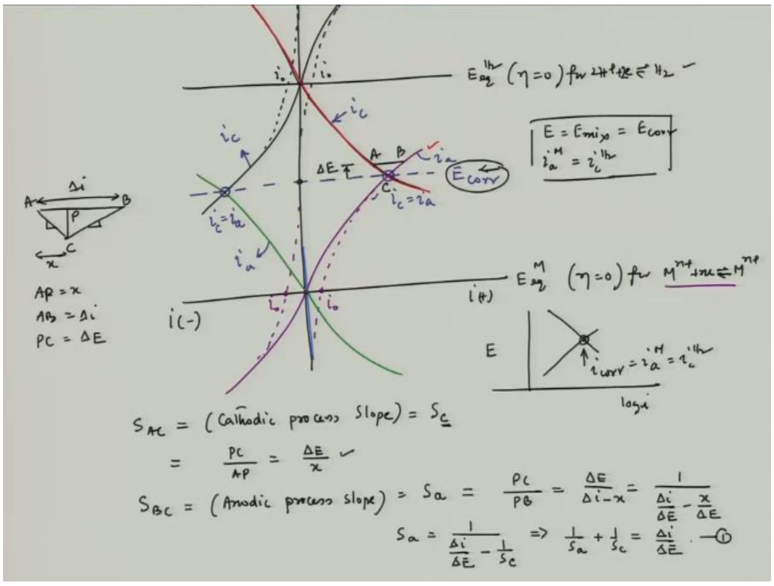
So then, if you see this, at this condition as well as this condition, ic + ia. Here also, ic + ia. Since this becomes ic in this case; and in this case, this becomes ic; and this is ia; and this is ia. So, it is basically, since the green one is the mirror image of this line. And this is the mixed potential. So, this potential becomes E corr. Now, this is the plot what we get. And, if I take a small, so that is, this will be the steady potential will reach, steady state potential where the rate of cathodic reaction equal to rate of anodic reaction.

But remember, this is for 2 different processes. One is the rate of cathodic reaction indicates the rate of hydrogen evolution reaction on the metal surface; and rate of anodic reaction indicates the metal dissolution rate. And that is what we are getting this steady condition. So now, if I take a small voltage perturbation around this. So, let’s say this is my small voltage perturbation, which is del E.

So, I can have a, like this. So now, that case, let’s say I commit as A, B, C. So, this becomes a triangle. So, at this, if I draw this triangle. So, this is my triangle ABC. Now, for this, I can; So, this is my, let’s say this is del i. And this particular point is, let’s say P. So, AP is x; let’s say this particular length is x. So then, I can; so, AP AC; AP = x; AB = del i; PC + del E. So, these are the; so, that means, I can see that this axis is i positive; this is i negative.

And after we leave that particular system in an electrolyte, I will reach this steady condition here. So, the polarization will be with reference to this potential. So now, that is what I have polarized it, a very small quantity del E towards anodic side. Now, if I try to do little bit of slope calculation; so now, I can take a slope, let's say slope of AC.

(Refer Slide Time: 22:50)



$$S_{AC} = (\text{Cathodic process Slope}) = S_c = \frac{PC}{AP} = \frac{\Delta E}{x}$$

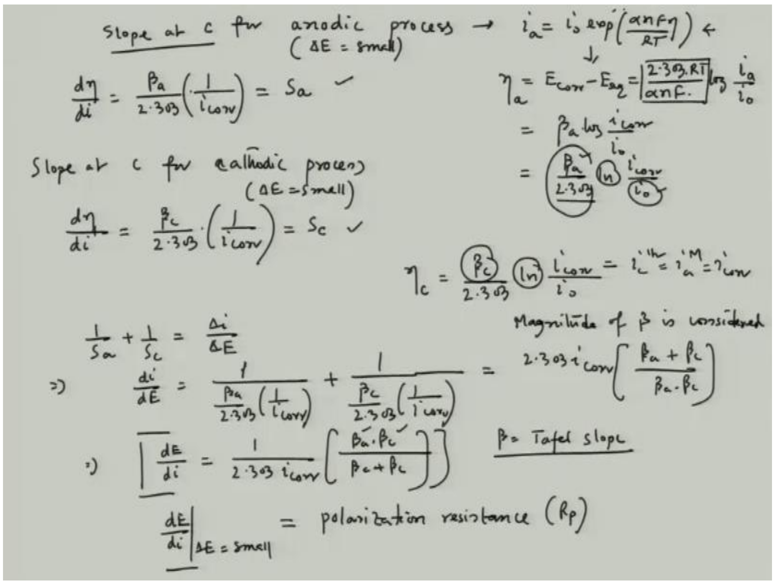
$$S_{BC} = (\text{Anodic process slope}) = S_a = \frac{PC}{PB} = \frac{\Delta E}{\Delta i - x} = \frac{1}{\frac{\Delta i}{\Delta E} - \frac{x}{\Delta E}}$$

$$S_a = \frac{1}{\frac{\Delta i}{\Delta E} - \frac{1}{S_c}} \Rightarrow \frac{1}{S_a} + \frac{1}{S_c} = \frac{\Delta i}{\Delta E} \quad \text{—①}$$

So, that slope, that is this slope we are trying to measure. So, that is the slope of cathodic process slope. So, this I can write it as PC divided by AP, which is nothing but del E by x. Similarly, I can have a slope of this line. So, S BC; so, which is the anodic process slope. So, I can write it is as Sc; c means cathodic. This, I can write it as Sa; this mean anodic. So, this becomes PC divided by PB, which is nothing but ΔE /(Δi - x).

So, I can do little bit of juggling. So, I can, 1/{(Δi/ΔE)-(x/ΔE)}. And we see that, this is nothing but Sc. So, I can write Sa =1/{(Δi/ΔE)-(1/Sc)}. Sorry, this becomes Sc. So, I can write {(1/Sa) + (1/Sc)} = (Δi/ΔE). So, this is one important relation, let's say equation 1. Now, I can again look at this particular picture. So now, at this point, if I try to find out the slope at this point; and since this is at a very high over voltage compared to the equilibrium potential for the metal reaction. So, that means, this will be close to ia. So, ia + i applied.

(Refer Slide Time: 25:46)



Slope at c for anodic process → $i_a = i_o \exp\left(\frac{\alpha n F \eta}{RT}\right)$ ←
(ΔE = small)

$$\eta_a = E_{corr} - E_{eq} = \boxed{\frac{2.303 RT}{\alpha n F}} \log \frac{i_a}{i_o} = \beta_a \log \frac{i_{corr}}{i_o} = \frac{\beta_a}{2.303} \ln \frac{i_{corr}}{i_o}$$

$$\frac{d\eta}{di} = \frac{\beta_a}{2.303}\left(\frac{1}{i_{corr}}\right) = S_a \checkmark$$

Slope at c for cathodic process
(ΔE = small)

$$\frac{d\eta}{di} = \frac{\beta_c}{2.303}\left(\frac{1}{i_{corr}}\right) = S_c \checkmark$$

$$\eta_c = \frac{\beta_c}{2.303} \ln \frac{i_{corr}}{i_o} = i_c^{H} = i_a^{M} = i_{corr}$$

$$\frac{1}{S_a} + \frac{1}{S_c} = \frac{\Delta i}{\Delta E}$$

Magnitude of β is considered

$$\Rightarrow \frac{di}{dE} = \frac{1}{\frac{\beta_a}{2.303}\left(\frac{1}{i_{corr}}\right)} + \frac{1}{\frac{\beta_c}{2.303}\left(\frac{1}{i_{corr}}\right)} = 2.303\, i_{corr}\left(\frac{\beta_a + \beta_c}{\beta_a \cdot \beta_c}\right)$$

$$\Rightarrow \frac{dE}{di} = \frac{1}{2.303\, i_{corr}}\left(\frac{\beta_a \cdot \beta_c}{\beta_a + \beta_c}\right)$$

β = Tafel slope

$$\left.\frac{dE}{di}\right|_{\Delta E = small} = \text{polarization resistance } (R_p)$$

So now, if I try to find out slope at this particular point, so that slope at C for anodic process. So, that means, I have to find a slope for this i + RT 2.303αnF. So, I have to find out

$$i = i_o\, exp\; exp\; \left(\frac{nF\eta}{RT}\right)$$

So, this equation, I have to use, just to find out slope at C for the anodic process. So, that case, I can write this equation as

$$\eta = E_{corr} - \ E_{eq} = \ \frac{2.303RT}{\alpha nF} log\; log\; \left(\frac{i_a}{i_o}\right) = \ \beta_a\ \ log\; log\; \left(\frac{i_a}{i_o}\right)\ = \beta_a\ log\; log\; \left(\frac{i_{corr}}{i_o}\right)$$

Since, at this point, at this location, ia + i corr + ic. This is hydrogen; this is metal. So, this is metal. Now, if I do d di which will be; I can also write it as β_a 2.303 ln (i_{corr}/ i_o). So then, I can write this one as beta 2.303, 1 by i corr. Since i zero is constant, this is constant, this is also; this entire part is constant, this is constant.

So then, this becomes this. So, this is nothing but Sa. Similarly, slope at c for cathodic process. And here, one more is when del E is equal to small. And this is del E equal to small. So, that time, d neeta by di would be β_c 2.303 (1/i_{corr}). Since neeta; and this becomes neeta a of course.

$$\eta_c = \frac{\beta_c}{2.303}\, ln\; ln\; \left(\frac{i_{corr}}{i_o}\right)$$

And remember, we are taking everything in the log term.

So; and beta c, because of course we will be have 2.303 added. So, that is what 2.303, we are taking it in the denominator. So now, this is nothing but Sc. So now, if I put this in this equation;

put this 2 things, this one and this one in this equation 1. So, (1/Sa) + (1/Sc) = (Δi/ΔE). So, then I can write it as

$$\frac{\Delta i}{\Delta E} = \frac{1}{\frac{\beta_a}{2.303}\left(\frac{1}{1_{corr}}\right)} + \frac{1}{\frac{\beta_c}{2.303}\left(\frac{1}{1_{corr}}\right)}$$

And here, I corr I can put, because i c hydrogen + ia metal + i corr. So, another thing is, in case of beta c, we are considering, we are just considering the magnitude. Magnitude of beta is considered. Since, this negative sign just indicates the direction of current flow, the cathodic current flow. So, if we do simplification; so then,

$$\eta_c = 2.303\ i_{corr}\left[\frac{\beta_a + \beta_c}{\beta_a * \beta_c}\right]$$

So then,

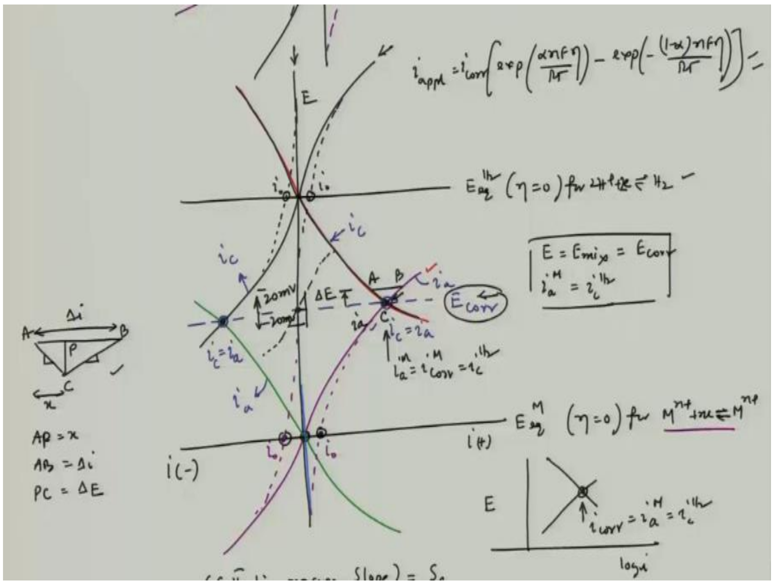
$$\frac{\Delta i}{\Delta E} = \frac{1}{2.303\ i_{corr}}\left[\frac{\beta_a * \beta_c}{\beta_a + \beta_c}\right]$$

And here, beta is Tafel slope. Fine. So now, this equation is a very vital equation. And this del E del i; when del E is equal to small; so, that time, this is considered as polarization resistance or Rp. And interestingly, if we know beta a and beta c, then we can find out the corrosion current density. But even if we do not know this beta n beta c, but doing a small experiment of fluctuating the polarization ±20 millivolt, we can get the slope for that particular linear line.

And that slope gives me, the polarization resistance. That means, the higher the polarization resistance, higher would be the corrosion resistance. Because, the more the polarization resistance lower would be the possibility of ion formation and higher would be the corrosion resistance. So, that is what, Rp gives an relative behavior. So, if 2 metals we consider in a simple, in an electrolyte; then if 1 metal has got a very high Rp, we can definitely say that, that metal has got a very high corrosion resistance in that particular solution.

And if we know beta n beta c for the, both the metals, then of course we can calculate the conversion rate in the form of i corr. And how do we do it if we get to this particular plot again. So, this Butler-Volmer equation can be modified.

(Refer Slide Time: 34:04)



Instead of i applied, we were having $i_o \exp(\alpha nF\eta/RT)$ + exponential. So, this was the equation we have considered. Now there, instead of i zero, if we put i corr, we could see that, that equation is validated. Because, here it was i zero in this particular case. And in this hydrogen case, this was the i zero. But, at this steady state E corr potential, I could see that these 2 current densities are also equal.

So, I could have an equation or equivalent equation for these 2 cases, anodic and cathodic cases at steady state E corr. And then, if I try to plot this one at a small over voltage with respect to this and this; so, then I can, my plot would be like this. Okay. And this particular voltage gap difference would be 20 millivolt. And here it is - 20 millivolt. And then, I can find out the slope at this particular point, where over voltage is zero corresponding to E corr.

And then, we can find out the parameter which is Rp. So, this is about the linear polarization. It gives us a quick measurement of corrosion rate of a metal in an electrolyte, just by measuring this linear portion of the corrosion, this Butler-Volmer equation at E corr with a ±20 millivolt over voltage. And then finding slope at over voltage zero. And that would be the linear polarization resistance.

Higher the linear polarization resistance, higher would be the corrosion resistance of a metal in an electrolyte. So, that is it. Let's stop here. We will now, next lecture onwards, we will talk about high temperature oxidation. Thank you very much.